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(54) Title: METHOD FOR THE PREPARATION OF PROTECTIVE COATINGS HAVING ENHANCED CHARACTERISTICS**(57) Abstract**

The present invention discloses a method for the preparation of heat-resistant protective coatings wherein powder-based compositions are cured at temperatures greater than about 250 °C to form high-film-build coatings which are substantially free of coating defects.

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**METHOD FOR THE PREPARATION OF PROTECTIVE COATINGS
HAVING ENHANCED CHARACTERISTICS**

Field Of The Invention

5 The present invention relates to a thermoforming heat-resistant powder coating composition. Specifically, the present composition provides a coating that can be applied at high-film-build to articles. More specifically, it relates to a method wherein powder-based compositions are applied at a high-film-build and cured at temperatures greater than about 205°C to form protective coatings which are substantially free of
10 coating defects.

Background Of The Invention

Powder coating compositions are well known and established art. A variety of articles are routinely powder coated by dipping, or tumbling them in a suspended or
15 static bed of resinous powder coating or by spray or sprinkling. The article on which the coating is applied is then heated to form a cured powder coating. These coatings have been shown to be particularly useful on metal surfaces including steel, aluminum and iron.

Various powder coating compositions are available that have been used in
20 heat-resistant applications. For example, it is known in the art that aromatic epoxy resins are used to provide good heat resistance. Epoxy compositions or epoxy and silicone mixtures have also been used in the industry for the same purpose. An example of a silicone coating composition is shown in U.S. Patent No. 5,433,396 (Daly et al.). However, this composition, along with the other silicone based powder
25 coating compositions, rely on the condensation of the silicone resin with another resin or itself to form the coating composition.

Additional references which describe the preparation of heat-resistant protective coatings are described below:

U.S. Patent No. 4,877,837 (Reising et al.) discloses powder-based
30 compositions comprising glycidyl functional acrylic polymers admixed with silicone having hydroxyl functional groups. The compositions may contain additives such as

flow agents, outgas agents and filler pigments (i.e., hydrated silicates of aluminum and calcium metasilicate) and are cured at a temperature between 180°C - 200°C).

U.S. Patent No. 4,446,259 (Vasta) discloses coating compositions in a liquid carrier, which can be cured at ambient temperatures, comprising glycidyl functional acrylic polymers admixed with a reactive polysiloxane. The coatings may contain additives such as metal oxides, metallic pigments and trace amounts of multivalent metal ions including tin and zinc. Vasta also discloses fluorocarbon-based powder compositions which are baked at 200°C - 345°C for about 2 hours to provide a coating 25-75 microns thick.

10 Other related patents include: U.S. Patent No. 4,404,042 (Okada et al.); U.S. Patent Nos. 4,657,963 and 4,746,568 (Matsumoto et al.); U.S. Patent No. 5,442,396 (Daly et al.); U.S. Patent No. 4,879,344 (Woo et al.); and U.S. Patent No. 5,087,286 (Fukuda et al.).

15 A drawback with the prior art references relates to the protective coatings appearance and protective nature when elevated temperatures are used to cure high-film-build powder-based compositions. For example, when said compositions are cured at elevated temperatures, condensation and thermal decomposition by-products often generate gases which can form pinholes, cracks and craters in the protective coating. These defects can be detrimental to coating properties including aesthetics, 20 heat resistance and corrosion resistance and typically limit the coating thickness to less than about 100 microns.

25 To enhance the performance characteristics of protective coatings, it is often necessary to apply a high-film-build. A higher-film-build generally allows complete deposition of the powders on a substrate and once cured, it increases the protective coatings film thickness to provide an extra barrier of protection.

Therefore, there remains a need for heat-resistant protective coatings which are characterized as having a film thickness greater than about 100 microns and are substantially free of coating defects.

30 **Summary Of The Invention**

The invention provides a thermoforming heat-resistant powder coating composition for use on metal substrates including steel, aluminum, iron and the like.

This composition further provides abrasion resistance and electrical resistance. It can be particularly useful for coating high temperature stacks, mufflers, manifolds, boilers, ovens, furnaces, steam lines, heat exchangers, barbecue equipment, cooking utensils and other parts that require a high heat resistance powder coating

5 compositions.

The present invention is directed to heat resistant protective coatings which are formed from powder-based compositions comprising:

- 1) at least one glycidyl-functional polyacrylic polymer;
- 2) at least one hydroxyl-functional polysiloxane;
- 10 3) at least one inorganic compound; and
- 4) at least one flow control agent;

wherein said composition is heated to a temperature greater than about 205°C to form a continuous film having a thickness greater than about 100 microns.

Surprisingly, the inventive coatings have excellent heat resistant

15 characteristics and pass the tape pull test method after about 500 hours at 340°C.

Additionally, the coatings outperform existing products currently available for use as heat resistant protective coatings. It is surmised that some of these unique characteristics can be attributed to the specific inorganic compounds and the temperature at which the powder-based compositions are cured.

20 In another aspect, the invention discloses a method for the preparation of heat resistant protective coatings comprising the steps of:

- 1) providing a dry blend of powder-based materials comprising:
 - a) at least one glycidyl-functional polyacrylate;
 - b) at least one hydroxyl-functional polysiloxane;
 - 25 c) at least one inorganic compound; and
 - d) at least one flow control agent;
- 2) melt mixing said blend and cooling to form solid particulate;
- 3) grinding said particulate to form a powder-based composition wherein said composition comprises an average particle size less than about 150
- 30 microns; and
- 4) coating said composition on a substrate and heating to a temperature greater than about 205°C.

Detailed Description Of The Invention

The protective coatings of the present invention are characterized as having increased heat resistance properties and are substantially free of coating defects when elevated film thicknesses are utilized. The coatings are particularly useful on articles which are subjected to elevated temperatures including stacks, mufflers, manifolds, boilers, ovens, furnaces, steam lines, heat exchangers, barbecue equipment and cooking utensils.

The glycidyl-functional polyacrylic polymers can be present in the powder-based compositions in a range from about 5.0% by weight to about 30.0% by weight, and preferably from about 10.0% by weight to about 20.0% by weight, based on the total composition solids. Examples of commercially available glycidyl-functional polyacrylic polymers include Fine-Clad™ A-244A from Reichold Chemicals, Inc. (Research Triangle Park, NC), and Almatex PD-7690 from Anderson Development Company (Adrain, MI). Said polymers may react with hydroxyl-functional compounds, through an addition mechanism, to form a crosslinked network.

Hydroxyl-functional polysiloxane can be present in the powder-based compositions in a range from about 20.0% by weight to about 50.0% by weight, and preferably from about 25.0% by weight to about 45.0% by weight, based on the total composition solids. Additionally, the polysiloxane can have hydroxyl-functionality in a range from about 1.0% by weight to about 10.0% by weight, and preferably from about 3.0% by weight to about 7.0% by weight, based on the total polysiloxane solids. The compositions may include hydroxyl-functional organo-siloxanes including dimethyl-based silicone polymers, diphenyl-based silicone polymers methyl-phenyl based silicone polymers and their mixtures. Examples of commercially available hydroxyl-functional polysiloxanes include Dow Corning® 1-0543, Dow Corning® 6-2230 and Dow Corning® Z-6018 from Dow Corning (Midland, MI); Wacker Silres® MK and Wacker Silres® SY-430 from Wacker Silicone Corp., (Adrien, MI); General Electric SR-355 from General Electric (Waterford, NY); and PDS-9931 from Gelest, Inc., (Tullytown, PA). Other suitable silicone-based polymers include those described in U.S. Patent No. 4,107,148 (Fujiyoshi et al.) and U.S. Patent No. 4,879,344 (Woo et

al.), incorporated herein by reference. Said polymers can self-condense and/or react with glycidyl functional polymers to form a crosslinked network.

Inorganic compounds can be present in the powder-based compositions in a range from about 10.0% by weight to about 70.0% by weight, and preferably from 5 about 20.0% by weight to about 40.0% by weight, based on the total composition solids. The preferred inorganic compounds are hydrated silicates of aluminum (mica), calcium metasilicate (wollastonite) and their mixtures. Commercially available pigments include Micro Mica[®] C-3000 from KMG Minerals (King Mountain, NC) and Nyad[®] 325 from Nyco (Willsboro, NY). It is surmised that the inventive coating 10 unique heat resistant properties can be attributed, in-part, to said compounds. For example, it is known that inorganic compounds are often used as fillers to increase the coatings volume and economics. Surprisingly, the present inventors have now discovered that mica and wollastonite significantly increase the coating heat resistance properties. Inorganic fillers such as zinc oxide, zinc borate, barium sulfate, calcium sulfate, calcium carbonate, hydrated silicate of magnesium and anhydrous sodium 15 potassium alumina silicate fail to increase the coatings heat resistance properties. It is further surmised that mica and wollastonite enhance the glycidyl-silanol addition reaction to form a substantially crosslinked network.

Flow control agents can be present in the powder-based compositions in a 20 range from about 0.2% by weight to about 3.0% by weight, and preferably from about 0.5% by weight to about 1.5% by weight, based on the total composition solids. The flow control agents may include acrylics, silicones and fluorine-based polymers. Examples of commercially available flow control agents include Resiflow P-67[™] and Clearflow Z-340[™] from Estron Chemical, Inc. (Calvert City, KY); Mondaflow[®] 2000 25 from Monsanto (St. Louis, MO); Modarez[®] MFP from Synthron, Inc. (Morgantown, NC); and BYK[®] 361 from BYK Chemie (Wallingford, CT). Said agents enhance the compositions melt-flow characteristics and help eliminate surface defects.

The powder-based compositions may contain additives including adhesion 30 promoters, degassing agents, catalysts, fillers, texturizers, coloring agents, plasticizers, surfactants and their mixtures.

If desired, adhesion promoters can be used in the powder-based compositions including epoxy-based polymers, silane-based polymers, phenolic resins, chlorinated

polyolefins and their mixtures. Examples of commercially available adhesion promoters include Araldite® GT-7013 and Araldite® GT-7220 from Ciba-Geigy corporation (Hawthorn, NY). The adhesion promoters may be present in a range from about 0.1% by weight to about 5.0% by weight, and preferably from about 1.5% by weight to about 3.0% by weight, based on the total composition solids.

5 Degassing agents can be used in the powder-based compositions and may be present in a range from about 0.1% by weight to about 5.0% by weight, and preferably from about 0.5% by weight to about 3.0% by weight, based on the total composition solids. Examples of a commercially available degassing agents include Uraflow B 10 from GCA Chemical Corporation (Brandenton, FL), Oxymelt A-2™ from ESTRON Chemical (Calvert City, KY), and Benzoin from Generichem Corp. (Little Falls, NJ). Said materials assist in the release of gases during the curing process.

15 Small quantities of catalysts may be used in the powder-based compositions which may include stannous octoate, dibutyl tin dilaurate, zinc octoate and their mixtures. Commercially available catalysts include Octaflow ST-70™ from ESTRON Chemical, Inc., (Calvert City, KY); and Actiron DBT™ from Synthron (Morgantown, NC). The catalysts may be present in a range from about 0.01% by weight to about 5.0% by weight, and preferably from about 0.1% by weight to about 3.0% by weight, based on the total composition solids. The catalysts are used to enhance the curing 20 characteristics of the powder-based compositions.

25 If desired, other inorganic fillers can be used in combination with the preferred inorganic compounds of the present invention. Suitable examples include zinc oxide, calcium carbonate, magnesium silicate (Talc), calcium sulfate, barium sulfate, zinc borate, anhydrous sodium potassium alumino silicate, calcium sulfate, calcium carbonate and their mixtures. A commercially available filler is Duramite® from ECC International (Atlanta, GA). The fillers may be present in a range from about 10.0% by weight to about 50.0% by weight, and preferably from about 20.0% by weight to about 40.0% by weight, based on the total composition solids. The fillers can be used to provide texture, control gloss and increase the coatings volume to enhance its 30 economics.

If desired, texturizers can be used in the powder-based compositions and include polytetrafluoroethylene, rubber, glass grit, talc and their mixtures. A

commercially available texturizer includes Shamrock SST-3 from Shamrock Technologies (Newark, NJ). The texturizer may be present in a range from about 1.0% by weight to about 10.0% by weight, and preferably from about 2.0% by weight to about 7.0% by weight, based on the total composition solids.

5 Coloring agents can be used in the powder-based compositions and any heat stable coloring agent may be used. The preferred coloring agents are carbon black and black mixed metal oxides. Commercially available coloring agents include Black No. 101 from the Shepard Color Company (Cincinnati, OH), and Special Black 100 from Degussa AG (Frankfurt, Germany). The coloring agent may be present in a
10 range from about 1.0% by weight to about 25.0% by weight, and preferably from about 5.0% by weight to about 15.0% by weight, based on the total composition solids.

Plasticizers may be used in the present invention to provide flexibility. Plasticizers may include polymeric resins, elastomers, waxes, oils and their mixtures.
15 The plasticizers may be present in a range from about 1.0% by weight to about 15.0% by weight, and preferably from about 5.0% by weight to about 10.0% by weight, based on the total composition solids.

Surfactants can be used and may include inorganic polyphosphates, organic polyacids, nonionic block copolymers and their mixtures. The surfactants may be
20 present in a range from about 0.5% by weight to about 3.0% by weight, and preferably from about 1.0% by weight to about 2.0% by weight, based on the total composition solids. The surfactants are useful as dispersing agents for the inorganic compounds and inorganic fillers.

Fluidizing agents can be used to improve the dry-flow characteristics of the
25 powder-based compositions. Examples include fumed silica, alumina oxides and their mixtures. The fluidizing agent can be present in a range from about 0.05% by weight to about 1.0% by weight, and preferably from about 0.1% by weight to about 0.5% by weight, based on the total composition solids.

In the inventive method, for the preparation of heat resistant protective
30 coatings, the powder-based materials are combined and agitated to form a dry blend. The blend is melt mixed in an extruder, at a temperature less than about 130°C, and cooled to form solid particulate. Fluidizing agents may be added at this stage of the

process to enhance the materials dry-flow characteristics. Preferably, the particulate is ground at a temperature less than about 20°C. Lower temperatures reduce melt coagulation and enhance the grinding process. The powder-based compositions can have an average particle size in a range from about 0.1 microns to about 500 microns

5 and preferably from about 30 microns to about 200 microns. Said compositions may be applied on a substrate through electrostatically spraying or with a fluidized bed method. The coated substrate is then heated to a temperature in a range from about 200°C to about 250°C, and preferably from about 210°C to about 240°C, and more preferably from about 210°C to about 225°C. It is generally known that elevated

10 temperatures can accelerate a materials reactivity. For example, a reference describing the frequency of bond formation is described in "Organic Chemistry", T.W. Graham Solomons, second edition, pages 139-141. Briefly, the collision theory of reaction rates describes how the rates of chemical reactions are directly proportional to the collision frequency. In the present invention, it is surmised

15 elevated temperatures increase the frequency and extent of addition and/or condensation reactions to form a crosslinked polymer matrix.

The protective coatings can have a film thickness in a range from about 25 microns to about 255 microns, and preferably from about 100 microns to about 200 microns. A higher-film-build can enhance the coating process and increase the

20 protective coatings film thickness to provide an extra barrier of protection. For example, during manual and automated spraying applications it is often necessary to deposit a high-film-build to assure a complete deposition of the particles on the substrate. Additionally, a protective coating comprising a film thickness greater than about 100 microns is preferred in that such a high-film-build can enhance the coatings

25 resistance to abrasion and environmental corrosives.

The protective coatings provide excellent heat resistant properties and are particularly useful on articles which are subjected to elevated temperatures including stacks, mufflers, manifolds, boilers, ovens furnaces, steam lines, heat exchangers, barbecue equipment and cooking utensils.

30 The present invention is further illustrated, but not limited to, the following examples.

Examples

The following test methods were used:

Tape Pull Test Method (TPTM)

5 Aluminum cast coupons were electrostatically sprayed with powder-based compositions and heated in an electric oven for 13 minutes at 218°C. The samples were subjected to a temperature between 340°C - 399°C and tested at about 40 hours and at about 500 hours. After heating, the samples were cooled to ambient room temperature and aged for at least one hour. The samples were then covered with a piece of Scotch® Brand "8919" tape from 3M Company (St. Paul, MN) and firmly 10 applied using hand pressure. The tape was quickly removed, using a 90° peel mode, and visually inspected for signs of coating failure. The protective coating passes the TPTM when said coating is not transferred to the tape.

Outgassing Test Method (OTM)

15 The OTM is used to determine the maximum film thickness at which a powder-based composition can be applied and cured without showing coating defects from escaping gases. A 10.16 cm x 30.48 cm steel panel was coated with a powder-based composition wherein the coating thickness was gradually increased from about 25 microns to about 255 microns. The panel was heated to a temperature of about 20 220°C for 13 minutes and visually inspected for defects. The protective coating passes the OTM, through visual examination, when said coating is free of defects including pinholes, cracks and craters.

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Example 1

Example 1 describes powder-based compositions, using various inorganic materials, which have been cured and evaluated using the tape pull test method (TPTM).

30 Base formulation:

Dow Corning® 1-0543	70.0 grams
Fine-Clad™ A-244-A	30.0 grams
Resiflow P-67™	1.5 grams

Uraflow B	1.0 grams
Black 101	20.0 grams

Inorganic materials described below:

PIGMENT	GRAMS	TPTM (340°C)
Hydrated Silicates of Aluminum/Calcium Carbonate	53/53	Pass >500 hours
Calcium Metasilicate	75	Pass >500 hours
Calcium Metasilicate/Hydrated Silicates of Aluminum	40/40	Pass >500 hours
Zinc Oxide	50	Failed <40 hours
Zinc Oxide	70	Failed <40 hours
Zinc Oxide	90	Failed <40 hours
Anhydrous Sodium Potassium Alumino Silicate	70	Failed <40 hours
Anhydrous Sodium Potassium Alumino Silicate	90	Failed <40 hours
Barium Sulfate	50	Failed <40 hours
Barium Sulfate	70	Failed <40 hours
Barium Sulfate	90	Failed <40 hours
Zinc Borate	50	Failed <40 hours
Zinc Borate	70	Failed <40 hours
Zinc Borate	90	Failed <40 hours
Magnesium Silicate	50	Failed <40 hours
Magnesium Silicate	70	Failed <40 hours
Magnesium Silicate	90	Failed <40 hours
Calcium Sulfate	50	Failed <40 hours
Calcium Sulfate	70	Failed <40 hours
Calcium Sulfate	90	Failed <40 hours
Calcium Carbonate	50	Failed <40 hours
Calcium Carbonate	70	Failed <40 hours
Calcium Carbonate	90	Failed <40 hours

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The data shows the presence of hydrated silicate of aluminum and/or calcium metasilicate significantly increase the protective coatings heat resistant properties, compared to other inorganic pigments, showing the utility of the invention.

10 Example 2

Example 2 compares the heat resistance and outgassing properties of the inventive coating (IF-6531) from H.B. Fuller Company (St. Paul, MN) with two

commercially available coatings from Morton (Reading, PA) and O'Brien (Houston, TX).

TEST	MORTON (99-7003)	O'BRIEN (SFB-601-H1)	H.B. FULLER (IF-6531)
TPTM - Failure at 340°C	<60 hours	<20 hours	>500 hours
Outgassing	76.0 Microns	89 Microns	203 Microns

The data demonstrates that the inventive coating has higher heat resistance
5 compared to the commercially available coatings. Additionally, the inventive coating
can be utilized at a film thickness greater than 100 microns, without the appearance of
coating defects, showing the utility of the invention.

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Claims

1. A heat resistant protective coating formed from a powder-based composition comprising:
 - 5 a) at least one glycidyl-functional polyacrylic polymer;
 - b) at least one hydroxyl-functional polysiloxane;
 - c) at least one inorganic compound; and
 - d) at least one flow-control agent;
- 10 wherein said composition is heated to form a continuous film having a thickness greater than about 100 microns..
2. The protective coating as described in Claim 1, wherein said composition is heated to a temperature in a range of from about 205°C to about 240°C.
3. The protective coating as described in Claim 1, wherein said coating is 15 characterized as having a film thickness in a range of from about 100 microns to about 200 microns.
4. The protective coating as described in Claim 1, wherein said polyacrylic polymer is present in the powder-based composition in a range from about 10.0% by weight to about 20.0% by weight.
- 20 5. The protective coating as described in Claim 1, wherein said hydroxyl-functional polysiloxane is present in the powder-based composition in a range from about 25.0% by weight to about 45.0% by weight.
6. The protective coating as described in Claim 1, wherein said inorganic compound is present in the powder-based composition in a range from about 25 20.0% by weight to about 40.0% by weight.
7. An inorganic compound as described in Claim 5, wherein said compound is selected from the group consisting of hydrated silicates of aluminum, calcium metasilicate and mixtures thereof.
8. The protective coating as described in Claim 1, wherein the flow-control agent 30 is present in the powder-based composition in a range from about 0.5% by weight to about 1.5% by weight.

9. The protective coating as described in Claim 1, wherein said coating is substantially free of coating defects and passes the tape pull test method after about 500 hours at 340°C.
10. An article comprising a heat resistant protective coating, on at least one surface of the substrate, comprising the reaction product of:
 - a) at least one glycidyl-functional polyacrylic polymer;
 - b) at least one hydroxyl-functional polysiloxane;
 - c) at least one inorganic compound; and
 - d) at least one flow-control agent;
- 10 wherein said coating is characterized as having a film thickness greater than about 100 microns.
11. The article as described in Claim 10, wherein said coating is substantially free of coating defects and passes the tape pull adhesion method after about 500 hours at 340°C.
- 15 12. A method for the preparation of heat resistant protective coatings comprising the steps of:
 - a) providing a dry blend of powder-based materials comprising:
 - i) at least one glycidyl-functional polyacrylate;
 - ii) at least one hydroxyl-functional polysiloxane;
 - 20 iii) at least one inorganic compound; and
 - iv) at least one flow control agent;
 - b) melt mixing said blend and cooling to form solid particulate;
 - c) grinding said particulate to form a powder-based composition having an average particle size of less than about 150 microns; and
 - 25 d) coating said composition onto a substrate and heating to a temperature greater than about 205°C.
13. The method as described in Claim 12, wherein said materials are dry blended at ambient room temperatures.
14. The method as described in Claim 12, wherein the melt mixing process is
- 30 accomplished at a temperature less than about 130°C.
15. The method as described in Claim 12, wherein the grinding process is accomplished at a temperature less than about 20°C.

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16. The method as described in Claim 12, wherein said composition is coated onto a substrate by electrostatically spraying.
17. The method as described in Claim 12, wherein said protective coating is characterized as having a film thickness greater than about 100 microns.

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<p>(54) Title: METHOD FOR THE PREPARATION OF PROTECTIVE COATINGS HAVING ENHANCED CHARACTERISTICS</p> <p>(57) Abstract</p> <p>The present invention discloses a method for the preparation of heat-resistant protective coatings wherein powder-based compositions are cured at temperatures greater than about 250 °C to form high-film-build coatings which are substantially free of coating defects.</p>			

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FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

INTERNATIONAL SEARCH REPORT

Internat'l Application No
PCT/US 96/19331

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D183/04 C09D133/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 275 051 A (GLIDDEN CO) 20 July 1988 see claims 1-13 see page 2, line 16 - line 34 see page 5, line 12 - line 33 ---	1
X	US 4 877 837 A (REISING JOHN C ET AL) 31 October 1989 cited in the application see claims 1-6 see column 5, line 4 - line 6 see column 6; example 3 ---	1

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *'A' document defining the general state of the art which is not considered to be of particular relevance
- *'E' earlier document but published on or after the international filing date
- *'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *'O' document referring to an oral disclosure, use, exhibition or other means
- *'P' document published prior to the international filing date but later than the priority date claimed

- *'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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1

Date of the actual completion of the international search

18 September 1997

Date of mailing of the international search report

30.09.97

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Authorized officer

Depijper, R

INTERNATIONAL SEARCH REPORT

Interr	nal Application No
PCT/US 96/19331	

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	DATABASE WPI Week 8315 Derwent Publications Ltd., London, GB; AN 83-35398k XP002041034 & JP 58 036 447 A (FUJIKURA CABLE WORKS LTD.) , 3 March 1983 see abstract --- US 4 589 999 A (VASTA JOSEPH A) 20 May 1986 see claim 1 --- US 4 446 259 A (VASTA JOSEPH A) 1 May 1984 cited in the application see claim 1 -----	1 1 1
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INTERNATIONAL SEARCH REPORT

Information on patent family members

Intell. ~~ial~~ Application No

PCT/US 96/19331

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0275051 A	20-07-88	US 5077354 A AU 601542 B AU 1023488 A JP 63182320 A	31-12-91 13-09-90 21-07-88 27-07-88
US 4877837 A	31-10-89	NONE	
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